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## Assessing the reactivity of sodium alkyl-magnesiates towards Quinoxaline: single electron transfer (SET) vs nucleophilic alkylation processes

Zoe Livingstone,<sup>a</sup> Alberto Hernán-Gómez,<sup>a</sup> Sharon E. Baillie,<sup>a</sup> David R. Armstrong,<sup>a</sup> Luca M. Carrella,<sup>b</sup> William Clegg,<sup>c</sup> Ross W. Harrington,<sup>c</sup> Alan R. Kennedy,<sup>a</sup> Eva Rentschler,<sup>b</sup> and Eva Hevia<sup>\*a</sup>

By exploring the reactivity of sodium butyl-magnesiate  $[\text{Na}(\text{THF})_6][\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{Bu})(\text{THF})]^-$  (**1**) supported by the bulky chelating silyl(bisamido) ligand  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$  ( $\text{Ar}^* = 2,6\text{-iPr}_2\text{-C}_6\text{H}_3$ ) towards Quinoxaline (**Qx**), the ability of this bimetallic system to effectively promote SET processes has been disclosed. Thus **1** executes the single-electron reduction of **Qx** affording complex  $[\text{Na}(\text{THF})_6]_2[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}_2\text{Mg}_2(\text{Qx}^*)_2]^{2-}$  (**2**) whose structure in the solid state contains two quinoxalyl radical anions  $\text{Qx}^\bullet$  stabilised within a dimeric magnesiate framework. Combining multinuclear NMR and EPR measurements with DFT calculations, new insights into the constitution of **2** in solution and its magnetic behaviour have been gained. Further evidence on the SET reactivity of **1** was found when it was reacted with nitroxyl radical TEMPO which furnished contacted ion pair sodium magnesiate  $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{TEMPO})\text{Na}(\text{THF})_3]^-$  (**4**) where both metals are connected by an alkoxide bridge, resulting from reduction of TEMPO. The role that the different ligands present in **1** can play in these new SET reactions has also been assessed. Using an amination approach, the Bu group in **1** can be replaced by the more basic amide TMP allowing the isolation of  $[\text{Na}(\text{THF})_6][\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}\text{Mg}(\text{TMP})]^-$  (**3**) which was characterised by multinuclear NMR and X-ray crystallography.  $^1\text{H}$  NMR monitoring of the reaction of **3** with **Qx** showed its conversion to **2**, leaving the hydrogen atoms of the heterocycle untouched. Contrastingly, using sodium homoalkyl magnesiate  $[\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3]$  (**5**) led to the chemoselective C2 alkylation of this heterocycle, suggesting that the presence of the steric stabiliser  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$  on the mixed-metal reagent is required in order to facilitate the **Qx** reduction.

### Introduction

Pioneered by Wittig in 1951,<sup>1</sup> alkali-metal magnesiates have evolved from mere curiosities to a new family of versatile organometallic reagents which finds widespread applications in organic synthesis.<sup>2</sup> Operating in a synergistic manner, these bimetallic systems can offer superior chemo- and regioselectivities and/or functional group tolerances to those of their monometallic counterparts.<sup>3</sup> Most of the reactivity studies have focused on using these reagents as metalating reagents (via Mg–H or Mg–X exchange processes)<sup>4</sup> as well as anionic transfer agents to unsaturated organic molecules.<sup>5</sup> Alkali-metal magnesiates are usually prepared *in situ*. However, recent structural and spectroscopic studies on

organometallic intermediates prior to electrophilic interception have provided extremely valuable information that has greatly contributed towards rationalising the special behaviour of these bimetallic systems.<sup>6</sup> This has been nicely illustrated by Mulvey and O'Hara who recently reported the first examples of directed *ortho-meta* and *meta-meta'* dimetalations of substituted arenes where the supramolecular structure of the magnesiate base templates the regioselectivity of the Mg–H exchange process.<sup>7</sup> Recently we have become interested in the reactivity of sodium magnesiates that are supported by the highly sterically demanding silyl-bis(amide)  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$  containing bulky 2,6-diisopropylphenyl side-arms ( $\text{Ar}^*$ ).<sup>8</sup> Probing the reactivity of these bimetallic systems towards 1,3-benzoxazoles we have found that at room temperature selective C2-magnesiation of *N*-methylbenzimidazole can be selectively accomplished.<sup>9</sup> Contrastingly, when reacted with benzothiazole a remarkable cascade activation process is initiated, involving a sequence of C–H metalation, C–C coupling, ring-opening and nucleophilic addition reactions, leading to the isolation of intricate molecular assemblies.<sup>10</sup>

<sup>a</sup> WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK. E-mail: eva.hevia@strath.ac.uk

<sup>b</sup> Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany.

<sup>c</sup> School of Chemistry, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU.

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Building on these initial findings, herein we extend our reactivity studies towards diazines, another fundamental family of *N*-heterocyclic molecules using Quinoxaline (**Qx**) as a case study. Substituted diazines are frequently present in natural products, biologically active molecules, pharmaceuticals and materials.<sup>9</sup> The selective functionalisation of these  $\pi$ -deficient aza-heterocycles via metalation approaches using polar organometallic bases such as organolithiums or lithium amides can be particularly challenging,<sup>12</sup> since side reactions such as nucleophilic additions and dimerisations can hardly be avoided, affording in many cases complicated mixtures of products.<sup>13,14</sup> Contrastingly, using lithium magnesiate (TMP)<sub>2</sub>Mg·2LiCl (TMP = 2,2,6,6-tetramethylpiperidide) in the presence of ZnCl<sub>2</sub>, Knochel has elegantly demonstrated that diazines, including **Qx**, can be regioselectively deprotonated in excellent yields.<sup>15,16</sup>

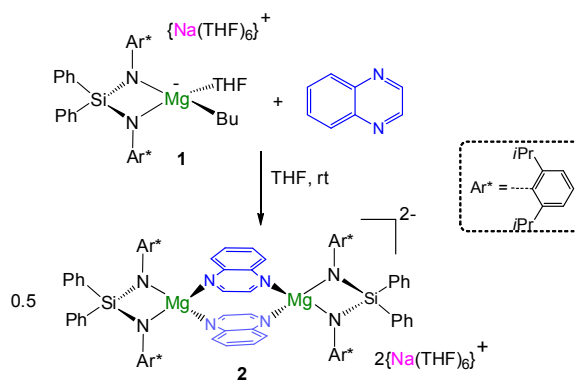
Intrigued by these precedents and aiming to advance the understanding of ligand effects in mixed-metal chemistry, here we provide a systematic study of the reactivity of **Qx** with the heteroleptic sodium magnesiates [Na(THF)<sub>6</sub>]<sup>+</sup>[{Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)Mg(R)(THF)]<sup>−</sup> (R = Bu, **1**; TMP, **3**), disclosing the ability of these bimetallic systems to promote single electron transfer (SET) reactions. The role that the sterically demanding ligand {Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)<sub>2</sub>}<sup>2−</sup> may play in these transformations was also assessed by contrasting these results with those observed when homo(alkyl) [NaMg(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>]<sup>17</sup> is employed.

## Results and discussion

### SET reactivity: trapping a quinoxyl radical anion in a magnesiate framework

Our studies started by reacting solvent separated sodium-magnesiate [Na(THF)<sub>6</sub>]<sup>+</sup>[{Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)Mg(Bu)(THF)]<sup>−</sup> (**1**) with one equivalent of **Qx** at room temperature in THF. The reaction takes place with a dramatic and almost instantaneous colour change of the solution (from light yellow to dark blue), which on cooling deposited blue crystals of [Na(THF)<sub>6</sub>]<sup>+</sup><sub>2</sub>[{Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)<sub>2</sub>Mg<sub>2</sub>(Qx\*)<sub>2</sub>]<sup>2−</sup> (**2**) as a THF disolvate in 55% yield (Scheme 1).

X-ray crystallographic studies of **2** revealed that no metalation of **Qx** has occurred (all H atoms of the anion including Qx rings could be located in difference maps). Instead **1** has reacted as a SET reagent, performing a one-electron reduction on a Quinoxaline molecule with the concomitant conversion of its butyl anion to Bu• radical which can be envisaged to dimerise to form octane.<sup>18</sup> Indeed using DFT calculations, the conversion of magnesiate **1** and **Qx** to give **2** and 0.5 equivalents of octane was found to be exergonic by 16.1 kcal mol<sup>−1</sup> (see ESI for details).



Scheme 1 Reaction of sodium magnesiate **1** with Quinoxaline (**Qx**)

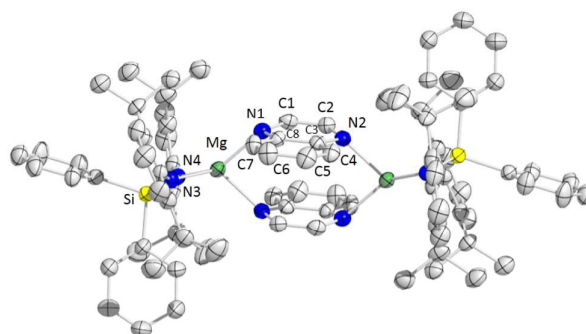
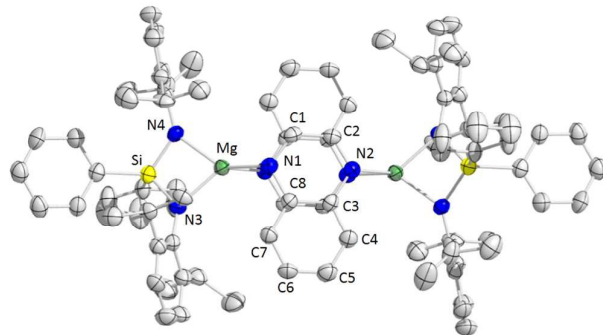


Figure 1 Structure of the anion of **2** with displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mg–N1 2.103(7), Mg–N2' 2.115(6), Mg–N3 2.028(6), Mg–N4 2.042(6), N1–C1 1.347(9), N1–C8 1.394(9), N2–C3 1.360(9), N2–C2 1.350(9), N1–Mg–N4 139.5(3), N1–Mg–N3 126.1(3), N3–Mg–N4 78.4(2), N1–Mg–N2' 84.1(2), N2'–Mg–N4 112.9(2), N2'–Mg–N3 120.0(3); the prime denotes an inversion-related atom.

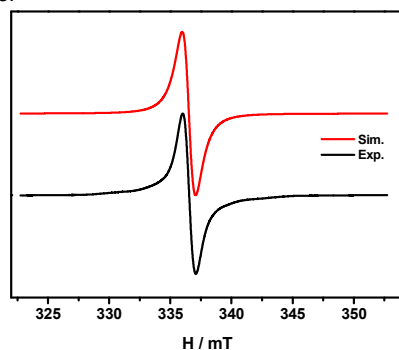
Solvent-separated ion-pair (SSIP) complex **2** comprises two {Na(THF)<sub>6</sub>}<sup>+</sup> cations and a novel centrosymmetric magnesiate dianion made up of two {Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)Mg} fragments connected by two Quinoxaline radical anions, where each of the N atoms of the heterocycle coordinates to a different Mg centre, closing a 10-membered {(MgNCCN)<sub>2</sub>} ring (Fig. 1). Interestingly, the two **Qx**\* rings are  $\pi$ -stacked in a transposed disposition in such a way that the parallel heterocyclic N<sub>2</sub>C<sub>4</sub> rings lie almost perfectly eclipsed while the C<sub>6</sub> rings are offset (Fig. 2). The N1...N2 distance between the two **Qx**\* rings is 2.825 Å, showing that these atoms are actually closer together than the pairs of eclipsed C atoms (separated by 3.033 and 3.034 Å). This is consistent with the pyramidalisation observed for both nitrogens (sums of the angles around N1 and N2 are 345.9 and 349.5° respectively). This arrangement suggests that the unpaired electrons of the **Qx**\* radicals are delocalised via the  $\pi$ -conjugated *p*-orbitals over the aromatic system, maximising their stabilisation by  $\pi$ - $\pi$  stacking interactions between the two C<sub>4</sub>N<sub>2</sub> rings. Reflecting the anionic constitution of the radicals, the Mg–N(**Qx**\*) distances in **2** (mean value, 2.109 Å) are intermediate between those reported by Hill for a series of  $\beta$ -diketiminato Mg complexes containing related *N*-heterocyclic molecules such as pyridine and quinoline<sup>19</sup> acting as neutral donors [i.e. Mg–N(pyridine), 2.174(3) Å]<sup>19a</sup> and

those found for Mg–N(amido) distances in **2** (N3 and N4 in Fig. 1, mean 2.035 Å).



**Figure 2** Alternative view of the structure of the anion of **2** (perpendicular to the mean plane of the atoms N1, N2, C1–C8) with displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity.

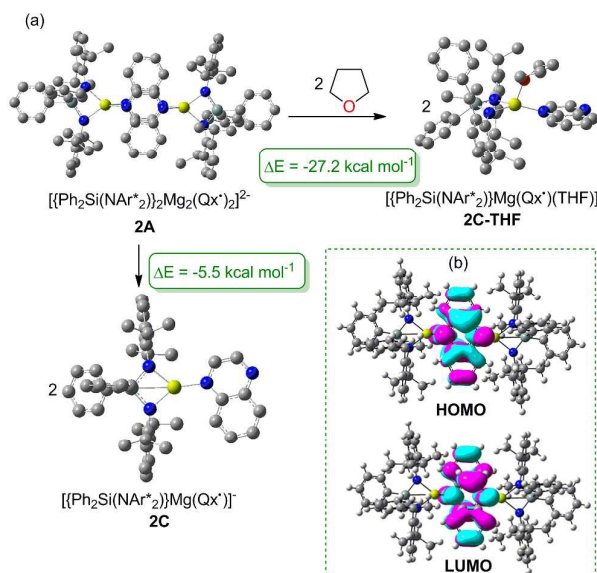
The good solubility of **2** in deuterated THF enabled its characterisation by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (see ESI for details). The most informative signals are those for the  $\text{Qx}^\bullet$  groups in the  $^1\text{H}$  NMR spectrum which are drastically shifted upfield [5.89 (2H) and 5.36 ppm (4H)] and significantly less well-resolved than those observed for free  $\text{Qx}^\bullet$  in the same deuterated solvent [8.82, 8.07 and 7.75 ppm (2H each)]. The radical-anionic character of the quinaxolyl ligand was confirmed by electron paramagnetic resonance (EPR) spectroscopy. EPR spectra of **2** in THF solutions collected at room temperature and at 105K (frozen solution) (Fig. 3)<sup>20</sup> showed a single signal which can be satisfactorily simulated assuming  $S = 1/2$  with an isotropic  $g$  value of 2.0 and a Lorentz line width of 1 mT. No hyperfine coupling to the N and H atoms was observed which differs from previous EPR studies on electrochemically generated non-coordinated quinaxolyl radical anions.<sup>21,22</sup>



**Figure 3.** EPR spectrum of **2** in THF at 105K

Interestingly, contrasting with these solution studies, variable temperature susceptibility measurements (from 2 to 300K) on solid samples of **2** revealed no paramagnetic behaviour, which suggests that the structure of this magnesiate in THF solutions must be different from that found in the solid state. For the latter scenario, the lack of paramagnetism can be attributed to a very strong antiferromagnetic coupling between the Quinoxaline radicals via  $\pi$ - $\pi$  stacking interactions which is consistent with the short distance found between the two N atoms of the two rings (2.825 Å) in the dimeric structure of the

dianion of **2** (*vide supra*). On the other hand, in THF solutions these dimers can be cleaved by the donor solvent, giving rise to monomeric THF-solvated  $[\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Mg}(\text{Qx}^\bullet)(\text{THF})]^-$  anions, where the possibility of antiferromagnetic coupling is no longer available. Supporting this interpretation, DFT calculations have shown that deaggregation of the dianion **2A** by two equivalents of THF to form two equivalents of monomer **2C-THF** is exothermic by 27.2 kcal mol<sup>-1</sup> (whereas in the absence of THF the process is significantly less energetically favoured,  $\Delta E = -5.5$  kcal mol<sup>-1</sup>) (Fig. 4). Furthermore, by modelling the structure of **2**, it was found that in agreement with the lack of paramagnetism observed experimentally, the singlet state model **2A** is 4.9 kcal mol<sup>-1</sup> more stable than that computed for **2B** with a triplet state configuration for the  $\text{Qx}^\bullet$  radicals.<sup>23</sup> Fig. 4 also shows the calculated HOMO and LUMO for model **2A** which are both based in the  $\pi$ -system of the quinoxalyl fragment with no contribution from the metals. DFT calculations also showed that the SOMO (defined as the highest singly occupied molecular orbital) of monomer **2C-THF** corresponds to the LUMO of free  $\text{Qx}^\bullet$  (Figure S24 in ESI and spin density calculated values).



**Figure 4.** (a) THF-mediated deaggregation of dianion **2A** into monomeric **2C**; (b) Calculated HOMO of models **2A**.

The formation of **2**, as the result of the one electron reduction of  $\text{Qx}^\bullet$  executed by sodium magnesiate **1** is truly surprising, since this bimetallic reagent has already shown its potential to act as a selective magnesiating reagent employing not only its butyl group but also its two basic  $\text{NHAr}^*$  amido arms.<sup>9,10</sup> It also contrasts with the straightforward formation of coordination adducts reported by Hill when  $\beta$ -diketiminato stabilised butyl magnesium complex  $[\text{HC}(\text{Me})\text{CNAr}^*]_2\text{MgBu}$  is treated with related  $N$ -heterocyclic substrates such as pyridine and quinoline.<sup>19</sup> Previous work by Fedushkin using Mg complexes supported by the also sterically demanding and dianionic ligand dpp-BIAN [1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene] has shown their



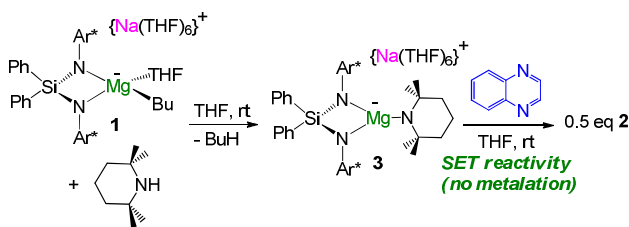
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ability to act as reducing agents towards aromatic ketones, although these reactions seem to be facilitated by the redox versatility of the dpp-BIAN ligand which can form stable adducts with Mg either as a dianion or as a radical monoanion.<sup>24</sup> A much closer precedent to the reactivity described here for **1** has been reported for the heteroleptic sodium zincate [(TMEDA)NaZn(TMP)tBu<sub>2</sub>] which facilitates the coupling of two chalcone molecules through their benzylic C positions via a SET process involving one tBu group attached to Zn.<sup>25</sup> Although we are not aware of any previous examples of structurally defined Mg complexes resulting from the reduction of Quinoxaline, it should be noted that Diaconescu has reported the double reduction of this N-heterocyclic molecule using a low-valent diuranium  $\mu\text{-}\eta^6, \eta^6$ -toluene complex which allows the isolation of a novel tetranuclear molecular quadrangle, with U(IV) vertices and reduced Quinoxaline as edges.<sup>26</sup>

Previous work by Knochel has shown that TMP-based mixed Li/Mg reagents can promote the regioselective  $\alpha$ -magnesiation of **Qx** in the presence of ZnCl<sub>2</sub>.<sup>15</sup> Furthermore, studies by Mulvey and O'Hara have revealed that the presence of sterically demanding and highly basic TMP groups as constituents of macrocyclic sodium magnesiate plays a major role in templating dimetalation processes of substituted aromatic substrates.<sup>7</sup> Building on these intriguing precedents, we pondered if a TMP-variant of sodium magnesiate **1** could be prepared, and whether it would favour the magnesiation of **Qx** over its one electron reduction.

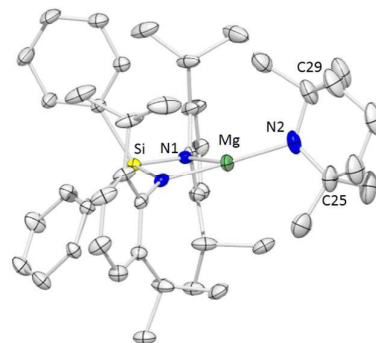
TMP magnesiate [Na(THF)<sub>6</sub>]<sup>+</sup>[Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)]Mg(TMP)]<sup>−</sup> (**3**) was prepared in a 71% yield using an amination approach by treating precursor **1** with the amine TMP(H) at room temperature (Scheme 2).



**Scheme 2** Synthesis of sodium TMP-magnesiate **3** and its reactivity towards Quinoxaline (**Qx**)

<sup>1</sup>H and <sup>13</sup>C NMR analysis of **3** in deuterated benzene solutions confirmed the substitution of the Bu group of **1** by a TMP anion. Thus an informative sharp singlet at 1.43 ppm is observed in the <sup>1</sup>H NMR spectrum for the Me groups of this amide which appears significantly deshielded relative to that observed for the parent amine TMP(H) (at 1.04 ppm). In addition the <sup>13</sup>C spectrum displayed four resonances at 51.4, 40.2, 35.9 and 20.1 ppm which can be assigned to the C $\alpha$ , C $\beta$ , Me and C $\gamma$  respectively of the Mg-TMP fragment (see ESI for details). The molecular structure of **3** was established by X-ray crystallographic studies (see Fig. 5 and ESI for details). Displaying a SSIP structure, **3** contains the same sodium cation as for **2** and for precursor **1**. Its magnesiate anion is made up by a distorted trigonal planar Mg centre (sum of angles around

Mg, 358.37°) which binds to the bidentate silyl-bis(amido) ligand [Mg–N1, 2.019(2) Å] and a terminal TMP group [Mg–N2, 1.967(4) Å]. This Mg–N(TMP) bond distance is rather shorter than that reported for the homoleptic anion of [Na(TMEDA)<sub>2</sub>]<sup>+</sup>[Mg(TMP)<sub>3</sub>]<sup>−</sup> (mean Mg–N, 2.050 Å),<sup>27</sup> which, as far as we are aware, is the only precedent in the literature of a TMP-magnesiate with a SSIP structure.



**Figure 5** Structure of the anion of **3** (disordered across a mirror plane) with displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mg–N1 2.019(2), Mg–N2 1.967(4), N1–Mg–N2 147.25(17), N1–Mg–N1' 79.28(11), N1'–Mg–N2 131.84(17), C25–N2–C29 117.2(4), C25–N2–Mg 118.4(4), C29–N2–Mg 123.9(3). The prime denotes a symmetry-equivalent atom.

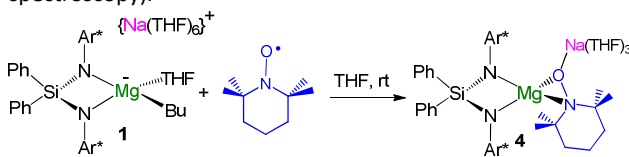
Structural and reactivity studies on the Turbo Hauser base (TMP)MgCl.LiCl have hinted at the basic activation of the TMP group when coordinated terminally to Mg.<sup>28,29</sup> This has been attributed to the fact that only one Mg–N bond needs to be broken to release the active base.<sup>28</sup> Interestingly, when **3** was treated at room temperature with **Qx**, a colour change of the solution from light yellow to dark blue similar to that described before in the formation of **2** is observed. Furthermore, <sup>1</sup>H NMR monitoring of the reaction showed a 52% of **3** to complex **2** after 72 hours (see Figure S20, ESI) without observing any evidence of a competing metalation process of **Qx** taking place. Although this reactivity pattern is quite unexpected, considering the relative acidity of the H-atoms in **Qx**,<sup>30</sup> O'Hara has recently demonstrated the ability of TMP anions to be involved in SET processes, by structurally defining the product of the reaction of radical 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) with a TMP-sodium zincate.<sup>25</sup>

#### Reactivity studies: SET to TEMPO and assessing the role of the supporting ligand {Ph<sub>2</sub>Si(NAr\*<sub>2</sub>)}<sup>2−</sup>

Further evidence on the SET reactivity of **1** was found when it was treated with the stable nitroxyl radical TEMPO. Finding widespread applications in radical chemistry,<sup>31</sup> TEMPO can act as a versatile ligand towards Mg amides<sup>32</sup> and other s-block metal systems,<sup>33</sup> retaining its radical nature or alternatively been reduced to its alkoxide TEMPO<sup>−</sup> anionic form. In both scenarios it can act as an O donor ( $\eta^1$ ) or as a N/O donor ( $\eta^2$ ). Within Mg chemistry, TEMPO has been successfully used as an organic oxidant to promote transition-metal free homocoupling reactions of Grignard reagents.<sup>34</sup> Furthermore, recent studies by Hill have uncovered the first example of

redox-based catalysis using a Mg complex for hydrogen release from silanes. Establishing the feasibility of SET reactivity on Mg catalysis, this process is based on a series of sequential TEMPO-mediated redox and Mg–O/Si–H metathesis transformations.<sup>35</sup> A 1:1 mixture of crystalline **1** and TEMPO was dissolved in THF and stirred at room temperature for an hour, affording a yellow solution that on cooling deposited colourless crystals of  $[(\text{Ph}_2\text{Si}(\text{NAr}^*)_2)\text{Mg}(\text{TEMPO}^-)\text{Na}(\text{THF})_3]$  (**4**) in a 41% yield.

A key aspect of this reaction is the reduction of TEMPO to its anionic form by complex **1** with the subsequent  $\text{Bu}^\bullet$  radical coupling to form octane.<sup>18</sup> Interestingly, reflecting the ability of TEMPO to act as a radical trapping reagent,<sup>36</sup> when **Qx** is treated with sodium magnesiate **1** in the presence of one molar equivalent of this nitroxyl radical, the formation of **2** is totally inhibited, affording instead **4** in almost quantitative yield (as evidenced by monitoring the reaction using  $^1\text{H}$  NMR spectroscopy).



Scheme 3 Reaction of sodium magnesiate **1** with Quinoxaline (**Qx**)

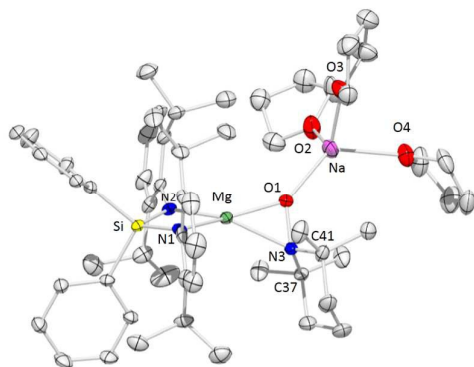


Figure 6: Molecular structure of **4** with displacement ellipsoids at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mg–O1 1.938(3), Mg–N1 2.035(4), Mg–N2 2.020(4), Mg–N3 2.160(4), N3–O1 1.467(4), Na–O1 2.237(3), Na–O2 2.300(5), Na–O3 2.271(5), Na–O4 2.330(5), O1–Mg–N1 151.23(15), N1–Mg–N2 78.88(15), O1–Mg–N3 41.50(12), N2–Mg–N3 139.76(15), N1–Mg–N3 128.20(16), O1–Mg–N2 127.02(15).

The molecular structure of **4** revealed a contacted ion pair (CIP) bimetallic motif where the two metals are connected by a TEMPO anion, which coordinates in an asymmetric fashion, using its N and O atoms (Figure 6). Thus while Mg experiences N–O chelation, the Na centre interacts only with the O of the TEMPO anion. By comparing the M–O(TEMPO) and N–O bond distances in **4** [1.938(3), 2.237(3) and 1.467(4) Å for Mg–O1, Na–O1 and N3–O1 respectively] with those reported in related complexes of these metals containing  $\mu_2$ -TEMPO anions,<sup>32,33,35</sup> it is clear that the ligand present in **4** is anionic as it must be for valency considerations.<sup>37</sup> Two examples of  $\eta^2(\text{N},\text{O})$ -coordination of TEMPO anions to Mg have been previously

reported in dimeric  $[\{\text{Mg}(\text{HMDS})(\text{TEMPO})\}_2]$ <sup>32</sup> and monomeric  $[(\text{dpp-BIAN})\text{Mg}(\text{TEMPO})(\text{THF})]$ <sup>38</sup>, displaying in both cases Mg–N bond distances that are noticeably elongated [2.395(3) and 2.2612(14) Å respectively] compared to that found in **4** [2.160(4) Å]. Understandably, this  $\eta^2(\text{N},\text{O})$  coordination mode to Mg imposes a severe distortion in its tetrahedral geometry [average bond angle, 111.10°; values range from 41.50(12) to 151.23(15)°]. As far as we can ascertain, **4** constitutes the first structurally defined intermediate of the reaction of an alkali-metal magnesiate with TEMPO, providing tangible evidence of the ability of these bimetallic systems to promote SET processes.

$^1\text{H}$  NMR spectroscopic studies of **4** in deuterated THF solution showed two informative broad singlets, each integrating for 6H, at 1.05 and 0.97 ppm for the Me groups of the TEMPO anion along with another three broader signals at 1.60, 1.52, 1.34 which can be assigned to the  $\beta$  and  $\gamma$ -H atoms respectively. These chemical shifts compare well with those previously recorded for other TEMPO complexes of s-block metals.<sup>33</sup> Turning to the  $^{13}\text{C}$  NMR spectrum, three resonances are observed at 59.6, 41.1 and 18.4 ppm for the C $\alpha$  and C $\beta$  and C $\gamma$  respectively along with other signals at 34.8 and 19.4 for two different methyl groups (see ESI for details). These spectroscopic data are consistent with hindered rotation around the N–O bond in the TEMPO anion, which can be expected to occur particularly if the Mg–N(TEMPO) and Mg–N(TEMPO) bonds observed in the solid structure of **4** persist in THF solutions.

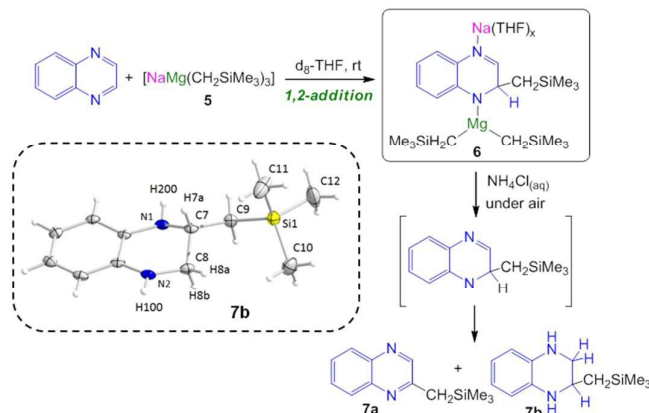
To assess the role that the supporting ligand  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$  plays in the formation of **2**, we also studied the reaction of **Qx** with the homo(alkyl) sodium magnesiate  $[\text{NaMg}(\text{CH}_2\text{SiMe}_3)_3]$  (**5**) (Scheme 4).<sup>17</sup> Contrasting with the reactivity of **1** and **3**,  $^1\text{H}$  NMR monitoring of the reaction revealed that no reduction of the heterocycle had occurred but instead the regioselective C2-addition of a monosilyl group across one of its C=N bonds was observed (Scheme 4*i*), forming heteroleptic magnesiate **6**.<sup>39</sup> Its  $^1\text{H}$  NMR spectrum evidenced the clear dearomatisation and loss of symmetry of the **Qx** ring, displaying five distinct CH resonances in the range 6.89 to 4.35 ppm (cf. Quinoxaline range 8.82–7.75 ppm). In addition two distinct sets of signals in a 2:1 ratio and at very distinct chemical shifts are observed for the monosilyl groups present in **6**. Thus, two resonances at -1.73 and -1.74 ppm can be assigned to the heavily shielded Mg-CH<sub>2</sub> groups (at similar chemical shift to that found for the same protons in trialkyl magnesiate **5**,  $\delta = -1.88$  ppm), whereas the CH<sub>2</sub> signals for the monosilyl group, that is now bound to another CH, appear as two multiplets at 0.37 and 1.00 ppm. Furthermore reflecting its change in hybridisation, the C atom that has undergone addition of the CH<sub>2</sub>SiMe<sub>3</sub> group in **6** resonates at 51.2 ppm in the  $^{13}\text{C}$  NMR spectrum, whereas in free **Qx** it appears at 146.2 ppm (see the ESI for spectroscopic details).

Hydrolysis of **6** under air renders the relevant dihydroQuinoxaline derivative that spontaneously disproportionates into a 1:1 mixture of the fully oxidised C2-substituted Quinoxaline **7a** and tetrahydro derivative **7b** (Scheme 4 *ii*). Both compounds have been fully characterised

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by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and in the case of **7b** its structure could be determined by X-ray crystallographic studies (Scheme 4 *iii*, see ESI for details). Illustrating the high levels of regioselectivity and efficiency of **5** towards **Qx**, the yield of this alkylation reaction to give a 1:1 mixture of organic products **7a–b** is 93% [determined by  $^1\text{H}$  NMR spectroscopy using ferrocene (10 mol%) as internal standard].<sup>40</sup>



**Scheme 4** (i) Reaction of sodium magnesiate **5** with Quinoxaline (**Qx**), (ii) hydrolysis under aerobic conditions, and (iii) molecular structure of reduced product **7b** with displacement ellipsoids shown at the 30% probability level.

The clearly contrasting behaviours of these related sodium magnesiates towards **Qx** point out that the SET reactivity exhibited by sodium magnesiates **1** and **3** must be favoured to a certain extent by the presence of the sterically demanding dianionic ligand  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$ . Previous studies have shown that far from being a mere spectator this ligand can be directly involved in the metalation of substrates such as benzothiazole<sup>10</sup> or pyrrole using one or two of its basic amido arms.<sup>9</sup> However, here, it seems to be acting as a stabilising support, providing steric shelter to the newly generated **Qx** $^{\bullet}$  radical anions (Figure S2 in ESI file for a space filling model diagram).

## Conclusions

Through the isolation and characterisation of novel sodium magnesiates **2** and **4** resulting from the one electron reduction of Quinoxaline (**Qx**) and TEMPO respectively, new insights into the ability of this important family of mixed-metal reagents to promote SET processes have been gained. For **2**, reactivity and theoretical studies have revealed the key role of the supporting ligand  $\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\}^{2-}$  on the mixed-metal reagent in order to stabilise and trap the **Qx** $^{\bullet}$  radical anions formed during the reaction. Thus, contrasting with previous reactivity studies in magnesiate chemistry, even when TMP-magnesiate **3**, which combines this silyl-bis(amido) ligand with a kinetically activated basic amido group, is employed the reduction of **Qx** occurs preferentially over its deprotonation. Contrastingly, using homoalkyl sodium magnesiate **5**, switches off the SET reactivity, promoting instead the chemoselective C2 alkylation of this heterocycle.

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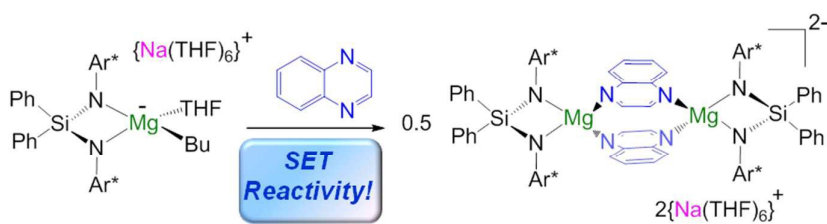
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## Graphical Abstract



## Text for TOC

*Structurally tracking the reaction of a sodium butylmagnesiatesilane supported by a highly sterically demanding silyl(bisamide) ligand towards quinoxaline, promotes single electron transfer (SET) reactivity.*